Electronic Supplementary Information

A Porous Metal-Metalloporphyrin Framework Featuring High-Density Active Sites for Chemical Fixation of CO_2 under Ambient Conditions

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Experimental Section

Synthesis of tetrakis(3,5-dicarboxybiphenyl)-porphine (H_{10}tdcbpp): This porphyrin ligand was synthesized according to reported procedures.[1]

Synthesis of MMPF-9: A mixture of tetrakis(3,5-dicarboxybiphenyl)-porphine (H_{10}tdcbpp) (2.0 mg), $Cu(NO_3)_2 \cdot 2.5H_2O$ (5.0 mg) and 1.0 mL mixed solvent (0.2 mL formic acid and 0.8 mL *N,N*-dimethylformamide (DMF)) was sealed in a Pyrex tube under vacuum and heated at 75 ^oC for 72 hours. The resulting dark red block-shaped crystals were harvested as synthesized (yield: 75 % based on H_{10}tdcbpp). The reaction was amplified to hundreds of milligrams quantity using multiple tubes.

Gas adsorption measurement: The gas adsorption isotherm was collected on the surface area analyzer ASAP 2020. Before the measurement, the freshly prepared sample was exchanged with methanol for 3 days. And then the sample of MMPF-9 was activated by supercritical CO_2 instrument according to the literature.[2] The N_2 adsorption isotherm was measured at 77 K using a liquid N_2 bath.

Catalysis experiments: In a typical reaction, the catalytic reaction was conducted in a Schlenk tube using the epoxide (25 mmol) with CO_2 purged at 1 atm under solvent free environment at room temperature catalyzed by MMPF-9 (0.03125 mmol, calculated based on copper paddlewheel units) or HKUST-1 (0.03125 mmol) and co-catalyst of tetra-*n*-tertbutylammonium bromide (TBAB, 0.58g) for 48 hours. The products were monitored by GC-MS (HP-5MS column, 5% phenyl methyl siloxane, 30 m × 0.25 mm × 0.25 μm; injector temperature 250 °C). All products were identified by the comparison of GC retention times and mass spectra with those of the authentic samples. For the recycling experiment, the reaction mixture was added with methanol and centrifuged for 5 min after the reaction. The liquid layer was siphoned out. And the residual solid was washed with methanol and centrifuged three times before being applied the same catalytic conditions.

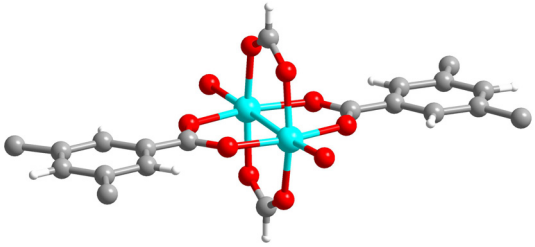

Fig. S1. The second type of copper paddlewheel units containing two coplanar formate ions.

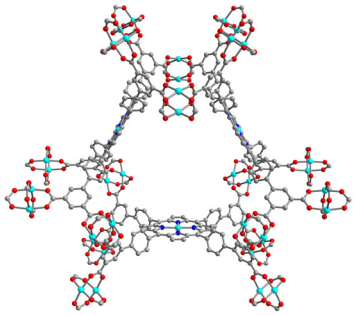

Fig. S2. Basic building block for the formation of truncated triangular channel.

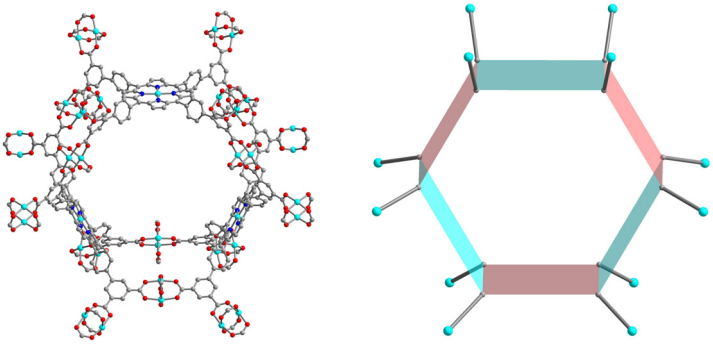

Fig. S3. Basic building block for the formation of truncated triangular channel (left) and simplified version as 12-connected nodes (turquoise balls as 4-connected node from first type copper paddlewheel units).

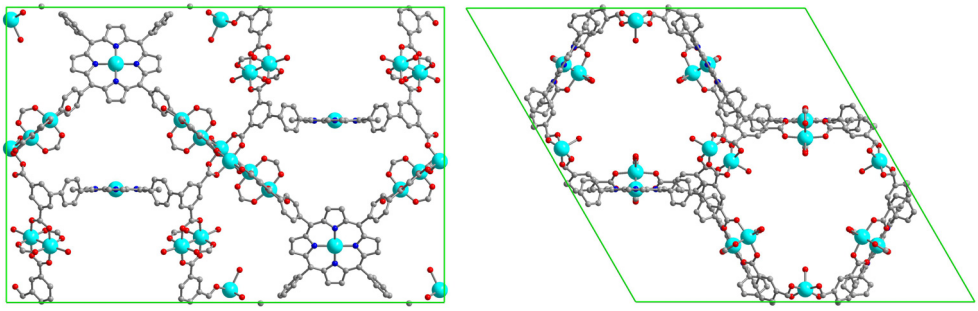

Fig. S4. Unit cell along *a* (left) or *b* (right) axis (copper sites are highlighted as turquoise balls).

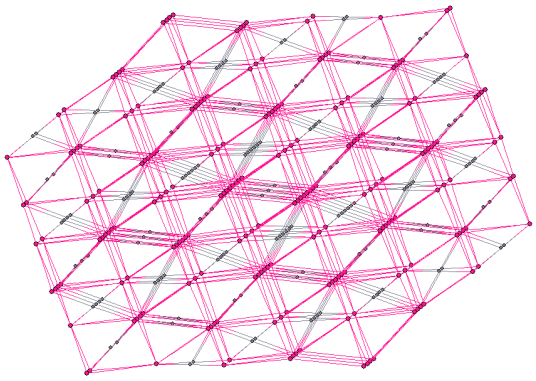

Fig. S5. (4, 12)-connected network of MMPF-9 (gray, 4-connected node; pink, 12-connected node).

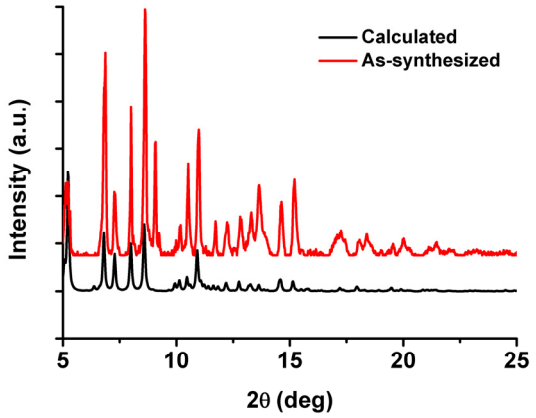

Fig. S6. Powder X-ray diffraction patterns of MMPF-9.

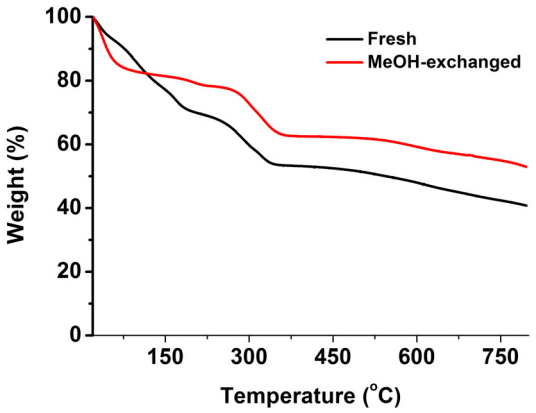

Fig. S7. Thermogravimetric analysis plots of MMPF-9.

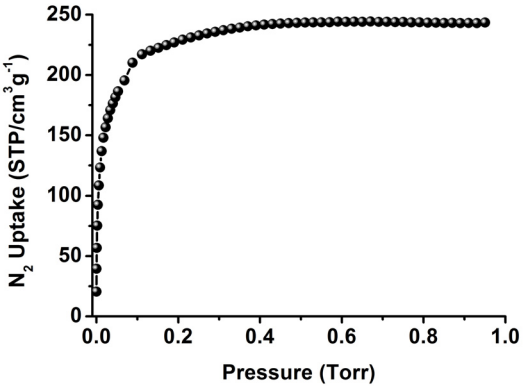

Fig. S8. N_2 adsorption isotherm of MMPF-9 at 77 K.

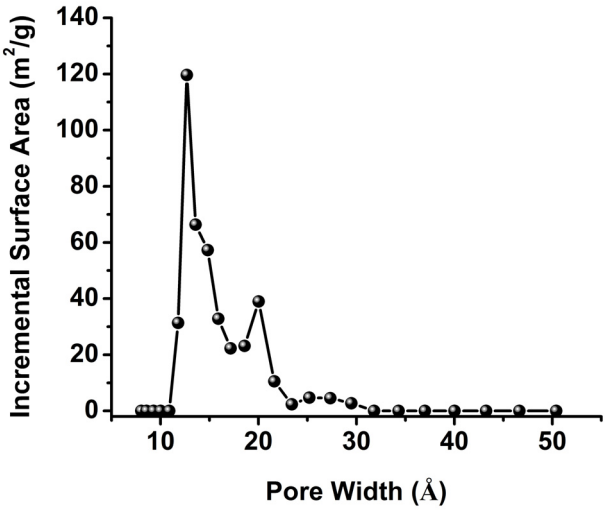

Fig. S9. Pore size distribution of MMPF-9 based on N_2 adsorption isotherm at 77 K (DFT model).

Single-Crystal X-ray Diffraction for MMPF-9

The single-crystal X-ray diffraction data for MMPF-9 was collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuK α , λ = 1.54178 Å). Indexing was performed using APEX2 (Difference Vectors method).[3] Data integration and reduction were performed using SaintPlus 6.01.[4] Absorption correction was performed by multi-scan method implemented in SADABS.[5] Space groups were determined using XPREP implemented in APEX2[3]. Structures were solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in WinGX[6,7,8,9] and OLEX2

programs.[10] Due to the presence of disordered solvent molecules in the structural voids, no high angle diffraction data have been observed and the diffraction data were observed only upon to 1.36 Å resolution. All non-H atoms were found in the difference Fourier map and were refined anisotropically. The restraints (DFIX, DELU and SIMU) have been used to refine the structure. And constraints for benzene rings (AFIX 66) in order to obtain chemically feasible model which would otherwise be distorted due to the lower resolution of diffraction data. The contribution of heavily disordered solvent molecules was treated as diffuse using Squeeze procedure implemented in Platon program.[11,12] Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in Table S1.

Table S1. Crystal data and structure refinement for MMPF-9	
Identification code	MMPF-9
Empirical formula	C_{80} H_{40} Cu_7 N_4 O_{30}
Formula weight	1981.94
Temperature	228(2) K
Crystal system, space group	Hexagonal, $P6_3/mmc$
Unit cell dimensions	*a* = 33.7831(10) Å *alpha* = 90 deg.
	b = 33.7831(10) Å *beta* = 90 deg.
	c = 43.456(3) Å *gamma* = 120 deg.
Volume	42952(3) Å ^3
Z, Calculated density	6, 0.460 Mg/m^3
Absorption coefficient	0.773 mm^-1
F(000)	5946
Crystal size	0.21 x 0.21 x 0.16 mm
Theta range for data collection	1.51 to 33.44 deg.
Limiting indices	-24<=h<=24, -23<=k<=24, -31<=l<=22
Reflections collected / unique	45388 / 3066 [R(int) = 0.0876]
Data / restraints / parameters	3066 / 84 / 272
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0485, wR2 = 0.1301
R indices (all data)	R1 = 0.0654, wR2 = 0.1354
Largest diff. peak and hole	0.90 and -0.65 e. Å ^-3

References.

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